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The regular cavities of zeolites form a unique environment for carrying out both stoichiometric and catalytic oxidation reactions. Transition metal ions such as molybdenum and cobalt may be introduced into the zeolite, and, as well, the acidity may be varied. As a continuation of previous work on the oxidation of olefins over Mo-Y zeolites it was demonstrated using shape selective poisons that the catalytic reaction actually takes place in the interior of the zeolite, rather than on the external surface of the crystallites. The role of cobalt-bipyridine-terpyridine complexes in forming reversible oxygen adducts was demonstrated. Although these complexes in zeolites have potential for the separation of oxygen from air, their value in oxidation catalysis is doubtful because in the presence of water the ligands are oxidized. The acidity of Y-type zeolites may be remarkably enhanced by removing aluminum from the framework. This acidity has been probed in a dynamic manner by studying acid-catalyzed reactions and

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by obtaining solid state NMR spectra of the basic molecules ammonia, trimethylamine and trimethylphosphine. The oxidation of trimethylphosphine to the corresponding oxide depends very much on the type of coordination in the zeolite. When coordinated to a Lewis acid site the base is readily oxidized at 25°C, but when coordinated to a proton in the zeolite the molecule is resistant to oxidation at temperatures in excess of 100°C.

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CATALYTIC OXIDATION BY  
TRANSITION METAL IONS IN ZEOLITES

FINAL REPORT

April 15, 1988

U.S. ARMY RESEARCH OFFICE

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## I. STATEMENT OF THE PROBLEM

The regular cavities within zeolites form a unique environment for carrying out both stoichiometric and catalytic oxidation reactions. Transition metal ions such as molybdenum, chromium and cobalt may be introduced into zeolites, where they form complexes with oxidants and substrate ligands. The ultimate goals of the project were (a) to understand oxidation reactions in zeolites at a molecular level and (b) to determine whether superior catalysts for certain oxidation reaction could be obtained by using selected combinations of metal ions and ligands in zeolites.

## II. SUMMARY OF IMPORTANT RESULTS

Synthesis, Characterization and Catalytic Properties of Mo-Zeolites: In earlier work under this contract considerable effort was devoted to the synthesis and characterization of Mo-Y zeolites. The catalytic properties of these materials for the epoxidation of cyclohexene and propylene were studied in detail. From XPS data it was evident that the molybdenum distribution within the zeolite paralleled the framework aluminum distribution; but one could not be sure that the catalytic reaction also occurred uniformly throughout the zeolite. Diffusional limitations within the zeolite were a potential problem, particularly since the reactions were carried out in the liquid phase, and the cavities of the zeolite were filled with a solvent. In order to resolve this question of external versus internal activity a technique known as shape-selective poisoning was employed. The epoxidation of cyclohexene was the test reaction, and to the zeolite slurry was added either tributylamine or triphenylamine. The former can easily enter the internal cavities of a Y-type zeolite, but the latter is excluded because of size. Activity data clearly demonstrated that tributylamine poisoned the active molybdenum, but triphenylamine did not. Thus, we concluded that the catalytic epoxidation reaction occurs primarily within the zeolite particles, rather than on the external surface.

Cobalt-Oxygen Complexes in Zeolite-Y: Oxygen adducts of cobalt complexes in zeolite-Y have been extensively studied in our laboratory because of their potential for the activation of molecular oxygen. The utility of the initial systems was limited by the fact that coordinated  $O_2$  attacked the ligands. It was subsequently found that a more stable mixed-ligand five-coordinated  $[Co^{II}(bpy)(terpy)]^{2+}$  ( $bpy$  = 2,2'-bipyridine,  $terpy$  = 2,2',2''-terpyridine) complex could be formed, but the yield relative to  $Co^{2+}$  was only 7%. More recently, by using  $Li^+$  as the other cation in the zeolite, yields of 45% have been achieved.

The mixed-ligand complexes are very convenient for the reversible coordination of  $O_2$ , and a stability constant of  $K_{O_2} = 2.9 \text{ torr}^{-1}$  at 298 K was measured for the reaction



This stability constant is large compared to those obtained for other solid-oxygen complexes. Moreover, the kinetics are suitable for effecting the separation of  $O_2$  from air, and separation factors of ca. 20 were easily obtained. These results suggest that the complex may be useful in practical separation processes.

The activation of  $O_2$  in this manner for a catalytic reaction is less promising because water, which is a product of hydrocarbon oxidation, modifies the complex. As suggested by Sargeson and co-workers, water converts the coordinated  $O_2^-$  to  $OOH^-$ . The hydroperoxy radical, which is a stronger oxidizing agent than the superoxide ion, attacks the ligands, and in this manner  $[Co^{II}(bpy)(terpy)]^{2+}$  is deactivated irreversibly. Preliminary attempts to oxidize hydrocarbons in a catalytic manner over  $[Co^{II}(bpy)(terpy)]^{2+}$  zeolites have not been successful.

Cobalt-Nitrosyl Complexes in Zeolite-Y: Another approach to the activation of  $O_2$  for the catalytic oxidation of organic substrates has been demonstrated in homogeneous systems by Diamond, Mares and co-workers and by Andrews and co-workers. This method involves a catalytic cycle in which a metal nitrosyl complex is oxidized with  $O_2$ , and the resulting nitro complex reacts with an organic substrate. In the process the nitro ligand is reduced back to a nitrosyl ligand.

We had previously investigated cobalt-dinitrosyl complexes in several zeolites and found that the NO could be oxidized to nitrito ligands with O<sub>2</sub>. More current research has shown that both nitrito and nitro ligands are formed in the zeolite, and that these may be used to oxidize 2-propanol to acetone. The coordinated NO<sub>2</sub> is reduced back to nitrosyl ligands, but the process is not completely reversible. Moreover, infrared spectra indicate that the propanol also becomes coordinated to the cobalt, and this inhibits the reoxidation of the nitrosyl ligands. Upon carrying out the reaction in a flow system at 70°C in which NO plus 2-propanol was introduced first, followed by O<sub>2</sub> and 2-propanol, a turnover number (TON) of about 3 was obtained in the presence of O<sub>2</sub>. Nevertheless, high selectivity to acetone was observed when O<sub>2</sub> and 2-propanol reacted over the catalyst. The system apparently is not catalytic because of the difficulty in reoxidizing the dinitrosyl complex.

A MAS-NMR Study of Acid Sites in Zeolite-Y: Acidity in zeolites may play a role not only in acid catalysis *per se*, but also in catalysis by transition metal complexes. The problem of measuring acidity in solids is difficult, although MAS-NMR spectroscopy applied to probe molecules appears to be a promising approach. In collaboration with Dr. William Earl of Los Alamos National Laboratory we carried out a MAS-NMR study of ammonia and trimethylamine (TMA) which interacted with Brønsted acid sites in a H-Y zeolite. By using <sup>15</sup>N-enriched materials adequate NMR spectra were obtained in a reasonable period. The NH<sub>4</sub><sup>+</sup> ions were formed at two sites which were distinct with respect to their chemical shifts. Excess ammonia in the zeolite interacted with NH<sub>4</sub><sup>+</sup> ions via hydrogen bonding, and this phenomenon induced further chemical shifts in the spectrum. Each form of NH<sub>4</sub><sup>+</sup> exhibited a different thermal stability which presumably reflects the acidity of the particular protonic site.

Trimethylphosphine also has been used to study the effect of zeolite acidity on the rate of oxidation. Resonances which result from the protonated adduct and the Lewis-bound base are quite different with respect to their chemical shifts. Whereas, the Lewis-bound (CH<sub>3</sub>)<sub>3</sub>P

was easily oxidized at 25°C to coordinated trimethylphosphine oxide, the protonated form  $[(CH_3)_3P-H]^+$  was resistant to oxidation at temperatures in excess of 100°C.

Dealuminated Zeolite-Y: The dealumination of zeolite-Y, either by steaming or by treatment with  $SiCl_4$  at elevated temperatures, has a profound effect on acidity as determined by probe reactions. During dealumination, framework aluminum is removed and the zeolite heals itself so that the final material is highly crystalline. Brønsted acid sites are, of course, associated with the framework aluminum, thus dealumination results in a decrease in the total acidity. But more significantly, the strength of the remaining acid sites greatly increased, as determined by the catalytic activity for hexane cracking or cumene dealkylation. The activity per framework Al atom increased ca. 20 fold upon decreasing the Al content from 51 to 34 atoms per unit cell.

The results support a model of Brønsted acidity in which protons associated with isolated framework aluminum (i.e. aluminum atoms for which only silicon is present in second-nearest tetrahedra) in the 4-rings gives rise to strong acidity. At about 33 Al atoms/unit cell there is a maximum number of Al atoms in such a configuration. In a very qualitative sense, the addition of more Al to the framework increases the negative charge, and therefore decreases the acidity. This concept is consistent with the theoretical calculations of Beran.

The relative inactivity of a normal H-Y zeolite is a surprising observation which appears to contradict previously published results. The difference may be attributed to variations in the mode of preparation. In our study care was taken to prevent dehydroxylation of the zeolite; whereas, in previous work dehydroxylation was extensive. As a result of  $^{29}Si$  NMR studies it now is known that extensive dehydroxylation results in dealumination, thus the earlier studies were actually carried out on dealuminated zeolites.

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### IV. PARTICIPATING SCIENTIFIC PERSONNEL

1. S. Imamura
2. J.R. Sohn
3. S.J. DeCanio
4. P.O. Fritz (graduate student - to receive degree in 1988).
5. S.E. Park
6. M. Zardkoohi (M.S. thesis based on this project)
7. D. Zalewski